

Study of reactions at metal oxide interfaces in aqueous solutions to 300°C

D. A. Palmer
D. J. Wesolowski
P. Bénézeth

Chemical and Analytical Sciences Division, Oak Ridge National
Laboratory, P.O. Box 2008, Oak Ridge TN 37831-6110, USA

The hydrogen-electrode concentration cell (HECC) was developed approximately 30 years ago at ORNL (Mesmer *et al.*, 1970) for the express purpose of making precise pH measurements in the laboratory to high temperatures (300°C) and salinities. During this time the thermodynamics of a wide variety of acid-base equilibria have been investigated in our laboratory in homogeneous aqueous phases as functions of temperature and ionic strength. Examples of such reactions are (1) the dissociation of inorganic and organic acids: H_2O , NH_4OH , CO_2 , NaHCO_3 , NaHSO_4 , NaB(OH)_4 , HCOOH , CH_3COOH , $\text{C}_6\text{H}_5\text{COOH}$, $(\text{COOH})_2$, $\text{CH}_2(\text{COOH})_2$, $(\text{CH}_2)_2(\text{COOH})_2$, $(\text{CH}_2)_2(\text{HOC})(\text{COOH})_3$, $\text{C}_6\text{H}_{11}\text{NH}_2\text{Cl}$, $(\text{CH}_2)_4\text{ONH}_2\text{Cl}$; $(\text{HOCH}_2)_3\text{CNH}_2\text{Cl}$, and $(\text{HOCH}_2)_3\text{CN}(\text{C}_2\text{H}_4\text{OH})_2\text{HCl}$; (2) metal ion hydrolysis: $\text{WO}_4^{2-}/\text{HWO}_4^-$; $\text{CrO}_4^{2-}/\text{HCrO}_4^-/\text{Cr}_2\text{O}_7^{2-}$; $\text{Al}^{3+}/\text{Al(OH)}^{2+}$, $\text{Mg}^{2+}/\text{Mg(OH)}^+$, and $\text{Fe}^{2+}/\text{Fe(OH)}^+$; metal complex formation: $\text{Fe}(\text{CH}_3\text{COO})_n^{2-n}$, $\text{Zn}(\text{CH}_3\text{COO})_n^{2-n}$, $\text{Cd}(\text{CH}_3\text{COO})_n^{2-n}$; $\text{Al}(\text{CH}_3\text{COO})_n^{3-n}$; FeCl^+ ; and $\text{Al}(\text{CH}_2(\text{COO})_2)_n^{3-2n}$. Studies continue in our laboratory and elsewhere on similar systems with recent emphasis on extending the temperature/pressure range of such measurements. The focus of this presentation is on the application of the HECC to investigations of heterogeneous systems.

Equipment

A number of versions of the HECC exist, however, one basic concept is intrinsic to them all, whether the cells are static (magnetically-stirred), or operate with a flow-through design. The fundamental principle of operation involves a relative measurement of hydrogen ion concentration using two hydrogen electrodes that are themselves the basis for potential measurements traceable to unit H^+ activity ($1/2\text{H}_2 \rightleftharpoons \text{H}^+ + \text{e}^-$). The standard cell configuration is as follows:



where HX or NOH represent known stoichiometric concentrations of acid or base in a supporting electrolyte medium, NX, and MY is the solute which imposes the pH to be measured on the test solution.

A recent modification of the static cell, which has provision for sampling the test solution containing a suspended solid and for the independent addition of two titrants, is shown in Fig. 1.

Solubility studies

Recently, the following solubility studies were undertaken with this HECC, viz.: brucite (Mg(OH)_2), Brown *et al.* (1996); boehmite (AlOOH); magnetite (Fe_3O_4); and zincite (ZnO) over the ranges of temperature: Mg(OH)_2 , 60–200°C; AlOOH , 100–290°C; Fe_3O_4 , 100–250°C; and ZnO , 50–290°C) Direct pH monitoring provides a sensitive measure of the attainment of equilibrium, and in the

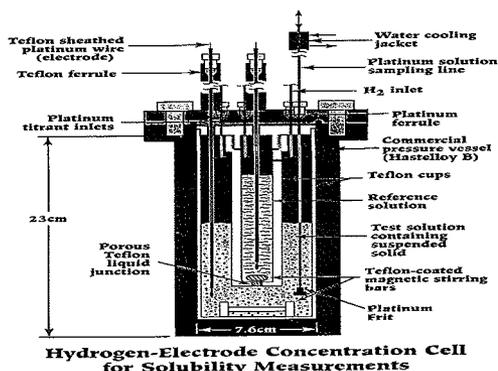


FIG. 1. Schematic diagram of a 'static' HECC.

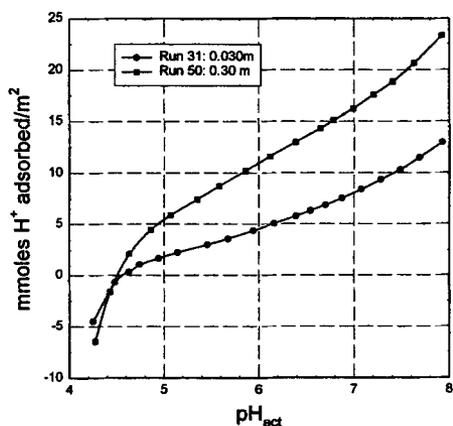


FIG. 2. Titration curves for magnetite in contact with a solution containing sodium trifluoromethane-sulphonate at 200°C.

case of boehmite these measurements have been used to determine the kinetics of the dissolution/precipitation reactions.

The solubility results for boehmite are the most extensive, extending to five molal ionic strength. The discussion here mainly will serve to demonstrate the viability of the experimental method, while establishing speciation generalities that simplify data treatment (Bénézeth *et al.*, 1997). The details of the corresponding zincite study will be presented by P. Bénézeth during this symposium (Wesolowski *et al.*, 1998). The magnetite study is still in progress, but preliminary data gathered at 150°C will be discussed to indicate some possible shortcomings of the method and to display the complexity of the chemistry observed.

Surface adsorption studies

The HECC has also been utilized to investigate the thermodynamics of surface adsorption/desorption of hydrogen ions on rutile (TiO₂), magnetite, and zincite to 290°C. The former was chosen for the initial study in view of its low solubility, which provided an ideal, unambiguous test case for this high temperature potentiometric approach (Machesky *et al.*, 1998). Details of this study will be given by M.L. Machesky at this conference. The decrease of the zero-point-of-charge as a function of temperature is systematic and could be modeled readily by application of the Stern three-layer model. The results of the corresponding zincite study showed similar, but less systematic trends that can be rationalized only qualitatively at the present time and will not be

discussed further here.

Hydrogen ion adsorption onto magnetite is of significance from the viewpoint of understanding the behaviour of metal oxide/water interfaces, but also for the relevance of surface charge to corrosion and adsorption of other ionic species in commercial hydrothermal systems, including conventional power plants. As in the rutile studies, the pH at which two isothermal titration curves conducted at differing ionic strengths intersect is considered to be the point-of-zero-charge for that surface, above which the surface is negatively charged and below which anions may be attracted to a positively-charged surface. An example of two such titration curves is shown in Fig. 2. An additional titration at an intermediate ionic strength will be performed in the future to confirm the tentative pH_{ZPC} for this solid of 4.45 at 200°C. The pH_{ZPC} values for magnetite decrease systematically with increasing temperature in a manner similar to the temperature dependence of 1/2pK_w, as was the case for rutile (Machesky *et al.*, 1998).

The effects of surface oxidation on the adsorption isotherms and solubility of the bulk solid have been observed during this research and can be rationalized by the formation of maghemite surface layers, and even the complete conversion of magnetite to hematite in acidic solutions under high hydrogen pressures (e.g. 20 bar).

Summary

An overview of recent experimental research carried out at ORNL utilizing the HECC to monitor pH *in situ* is presented for systems involving solid metal oxide phases in contact with aqueous solutions to temperatures not exceeding 290°C. The solubility of boehmite is discussed in detail and the hydrogen ion adsorption on magnetite is the other main focus of this presentation.

References

- Bénézeth, P., Palmer, D.A. and Wesolowski, D.J. (1997) *Geothermics*, **26**, 465–81.
- Brown, P.L., Drummond Jr., S.E. and Palmer, D.A. (1996) *J. Chem. Soc., Dalton Trans.*, 3071–5.
- Machesky, M.L., Wesolowski, D.J., Palmer, D.A. and Ichiro-Hayashi, K. *J. Colloid. Interface Sci.*, **200**, 298–309.
- Mesmer, R.E., Baes Jr., C.F. and Sweeton, F.H. (1970) *J. Phys. Chem.*, **74**, 1937–42.
- Wesolowski, D.J., Bénézeth, P. and Palmer, D.A. (1998) *Geochim. Cosmochim. Acta*, (in press).